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Effect of bond angle and dihedral angle disorder on diamagnetic susceptibility of tetrahedrally coordinated amorphous semiconductors

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Abstract : We study the effect of bond angle and dihedral angle disorder on the diamagnetic susceptibility (χ) of a model amorphous semiconductor by adopting a linear combination of hybrids formalism. We have constructed orthormal basis states for the disorder network by introducing distortion in bond angles and dihedral angles. We have used the disorder basis states in the expression for χ and adopted suitable averaging techniques to obtain χ in terms of disorder parameters, which shows interesting results.

Keywords : Amorphous semiconductors, diamagnetic susceptibility, tetrahedral semiconductors.

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1. Introduction

Amorphous semiconductors have continued to be important materials not only due to their technological applications but also due to their interesting properties [1,2]. For example, the diamagnetic susceptibility χ of Ge in the amorphous (*a*) phase is 2.7 times more than that in the crystalline (*c*) phase [3]. For Si, the diamagnetic enhancement is about 4.5 times [4]. In the case of III-V compounds, a small change in χ (around 110%) is predicted [5]. We have developed a chemical bond formalism for diamagnetic susceptibility of tetrahedral amorphous semiconductors by introducing bond angle distortions [5,6]. The dihedral angle is also an important parameter in estimating the electronic properties of amorphous semiconductors [7]. In the present paper we study the effect of dihedral angle distortion on the diamagnetic susceptibility of amorphous semiconductors.

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2. χ of the tetrahedrally coordinated model amorphous semiconductor

The pair of orbitals forming a bond at the nearest neighbouring sites I and II respectively can be written as

$$a_0^{\mathrm{I}}(\boldsymbol{r}) = \tfrac{1}{2}s(\boldsymbol{r}) + (\sqrt{3}/2)p_z(\boldsymbol{r})$$

$$a_0^{\mathrm{II}}(\boldsymbol{r}-\boldsymbol{d}_0) = \tfrac{1}{2}s(\boldsymbol{r}-\boldsymbol{d}_0) - (\sqrt{3}/2)p_z(\boldsymbol{r}-\boldsymbol{d}_0) \quad (1)$$

where site I is the origin and $\boldsymbol{d}_0$ is the bond length along j = 0, locating one of the four nearest neighbouring sites 2. The other three hybrids $a_1^{\mathrm{I}}(\boldsymbol{r})$, $a_2^{\mathrm{I}}(\boldsymbol{r})$ and $a_3^{\mathrm{I}}(\boldsymbol{r})$ at site I, oriented along j = 1, 2 and 3 bonds, can be generated from $a_0^{\mathrm{I}}(\boldsymbol{r})$ by making arbitrary rotations α_1, α_2 and α_3 about the y-axis followed by subsequent rotations Ψ_1, $(\Psi_2 + 2\pi/3)$ and $(\Psi_3 + 4\pi/3)$ about the z-axis, respectively using the D-representation of the full rotation group. Similarly the other three hybrids $a_j^{\mathrm{II}}(\boldsymbol{r}-\boldsymbol{d}_0)$ (j = 1, 2, 3) at $\boldsymbol{d}_0$ (site II) can be obtained in terms of arbitrary rotations β_1, β_2 and β_3 about the y-axis followed by subsequent rotations ϕ_1, $(\phi_2 + 2\pi/3)$ and $(\phi_3 + 4\pi/3)$ about the z-axis, respectively. We write α_j = α_T + γ_j and β_j = α_T + δ_j, where α_T = $\cos^{-1}$ (–1/3), *i.e.* the tetrahedral bond angle for the crystalline phase and γ_j, δ_j are distortions in bond angles.

We note that the bond angle is the angle subtended by two bonds at a common site, whereas the dihedral angle is the angle between the second neighbour bonds when projected on to a plane perpendicular to the common bond. From our construction of orbitals, the dihedral angle (ϕ) between hybrids , for example, $a_j^{\mathrm{I}}(\boldsymbol{r})$ and $a_j^{\mathrm{II}}(\boldsymbol{r}-\boldsymbol{d}_0)$ for j = 1, 2 and 3 is $(\pi + \phi_j - \Psi_j)$, where $(\phi_j - \Psi_j)$ is the distortion in the dihedral angle from the corresponding crystalline value π .We adopt a symmetric orthogonalization procedure [8] to obtain orthonormal sets of hybrids for each atomic site, say $\theta_j^{\mathrm{I}}(\boldsymbol{r})$ and $\theta_j^{\mathrm{II}}(\boldsymbol{r}-\boldsymbol{d}_0)$ in terms of the disorder parameters γ_j, Ψ_j and δ_j, ϕ_j, respectively [9]. We use these disorder basis states and obtain an expression for χ as a function of the disorder parameters γ_j, Ψ_j and δ_j, ϕ_j as [9]

$$\chi(\gamma_j, \delta_j, \Psi_j, \phi_j) = \chi_c + \chi_v(\gamma_j, \delta_j, \Psi_j, \phi_j) + \chi_p(\gamma_j, \delta_j, \Psi_j, \phi_j), \quad (2)$$

where χ_v is the Langevin-like diamagnetic term and χ_p is the Van Vleck-like paramagnetic term which depend upon the disorder parameters and χ_c is the core diamagnetic contribution. We write the distribution of dihedral angles as $P(\phi) = A\left[2/3\sin^2(3\phi/2) + 1/3\right]$, where ϕ is the dihedral angle and A is the normalization constant [7]. The dihedral angle distribution is symmetric about the staggered configurations (ϕ = π) of the crystalline phase at which the value is maximum. We carry out the configurational averaging of $\chi(\gamma_j, \Psi_j, \delta_j, \phi_j)$ by multiplying χ by the distribution functions $P(\pi + \phi_j)$ and $P(\pi + \Psi_j)$ for each orientation (j). Here Ψ_j is the distortion of the dihedral angle for site I with respect to the crystalline

configuration *i.e.* by considering ϕ_j = 0. Similarly the distortion ϕ_j which corresponds to that of site II is taken care of by considering Ψ_j = 0. The effect of bond angle disorder on χ is taken into account by a configurational averaging over the distribution of the bond-angle distortion γ_j, δ_j, *etc*. by considering a Gaussian type distribution function. Since γ_j, δ_j are small we neglect the higher order terms. In the averaging process terms containing γ_j^2, δ_j^2 survive. Thus we use the relation $<\gamma_j \gamma_{j'}> = <\delta_j \delta_{j'}> = \Delta\delta_{jj'}$, where $\delta_{jj'}$ is the Kronecker delta. The value of Δ can be interpreted as the root mean square bond angle distortation.

3. Results and discussion

We have computed the results of χ by including the effects of dihedral angle distortion and bond angle distortion. Since the values of the bond angle disorder parameter Δ is not available we take Δ = 0.03, 0.12 and 0.2 and study the trend. In Table 1, we present the results of χ of Si and Ge and III-V compound semiconductors for the amorphous phase. We note that the dihedral angle distribution function is maximum at the staggered configuration (crystalline phase) *i.e.* for Ψ_j = ϕ_j = 0. Therefore, if one does not take the dihedral angle distortion into account, the magnitudes of χ_v and χ_p become over estimated [9].

We note that χ_v contains matrix elements $\left\langle \theta_j^{\mathrm{I}}(\boldsymbol{r}) \middle| x^2 + y^2 \middle| \theta_j^{\mathrm{I}}(\boldsymbol{r}) \right\rangle$ and $\left\langle \theta_j^{\mathrm{II}}(\boldsymbol{r} - \boldsymbol{d}_0) \middle| x^2 + y^2 \middle| \theta_j^{\mathrm{II}}(\boldsymbol{r} - \boldsymbol{d}_0) \right\rangle$ which depend upon Δ for each bond orientation. However, the sum of the contributions due to all the four bond orientations turns out to be negligible. On the other hand, in χ_p, there is a factor $S^2/(1 - S^2)$, where S is the overlap integral which depends upon both the bond angle as well as dihedral angle disorder parameters. With increase in disorder, S decreases leading to decrease in the paramagnetic term χ_p. In case of elemental covalent semiconductors like Si and Ge, in the crystalline phase the values of χ_v and χ_p are individually large and nearly cancel. Therefore a small variation in χ_p changes drastically the net value of χ in the amorphous phase. However, in case of III–V compounds the magnitude of χ_v is much larger than χ_p in the crystalline phase. Therefore a small change in χ_p in the amorphous case does not affect much on the total magnetic susceptibility. As discussed above and also shown in Table 1, the diamagnetic enhancement in all the III–V compound semiconductors is within 105 to 108%. Whereas for group IV elemental semiconductors like Si and Ge the enhancement is 200% and 157% respectively. For better visualization of the quantitative and qualitative variation of the results, in Figure 1 we also present the variation of $\chi(\Delta)/\chi(0)$ as a function of Δ for Si, Ge and GaAs. We note that the diamagnetic enhancement first increases rapidly and then follows a monotonic path with increase in Δ.

Our analysis shows good agreement with the available experimental results [3,4]. Our results can be improved if one includes the effect of dangling bonds and wrong

Table 1. χ of model amorphous semiconductor.

Solid	Δ	χ_c	χ_v	χ_p	χ	$\chi(\Delta)/\chi(0)$ (%)
Si	0.00	–4.6	–39.3	37.5	–6.4	100
	0.03	–4.6	–35.89	31.40	–9.09	142
	0.12	–4.6	–35.37	28.81	–11.16	174
	0.2	–4.6	–34.93	26.75	–12.77	200
Ge	0.00	–16.6	–50.3	51.2	–15.7	100
	0.03	–16.6	–45.88	42.83	–19.65	125
	0.12	–16.6	–45.22	39.42	–22.40	142
	0.2	–16.6	–44.64	36.58	–24.66	157
GaP	0.00	–11.7	–46.4	28.1	–30.0	100
	0.03	–11.7	–42.43	23.69	–30.43	102
	0.12	–11.7	–41.91	21.91	–31.7	105
	0.2	–11.7	–41.45	20.48	–32.67	108
GaAs	0.00	–16.6	–47.4	30.7	–33.3	100
	0.03	–16.6	–43.31	26.29	–33.62	101
	0.12	–16.6	–42.77	24.51	–34.86	104
	0.2	–16.6	–42.3	23.03	–35.86	107
GaSb	0.00	–22.0	–67.2	41.9	–47.3	100
	0.03	–22.0	–61.45	35.75	–47.70	101
	0.12	–22.0	–61.02	34.17	–48.85	103
	0.2	–22.0	–60.03	31.13	–50.90	107
InP	0.00	–20.0	–50.9	29.2	–41.7	100
	0.03	–20.0	–47.05	25.14	–41.91	101
	0.12	–20.0	–46.48	23.58	–42.9	103
	0.2	–20.0	–45.96	22.26	–43.7	105
InAs	0.00	–25.0	–54.9	34.1	–45.8	100
	0.03	–25.0	–50.67	29.31	–46.36	101
	0.12	–25.0	–50.05	27.44	–47.61	104
	0.2	–25.0	–49.5	25.86	–48.64	106
InSb	0.00	–33.0	–71.3	41.8	–62.5	100
	0.03	–33.0	–65.71	35.77	–62.94	101
	0.12	–33.0	–64.91	33.34	–64.57	103
	0.2	–33.0	–64.2	31.32	–65.88	105

bonds due to odd membered rings (for amorphous III–V compounds) and also the effect of localized states in the formulation.

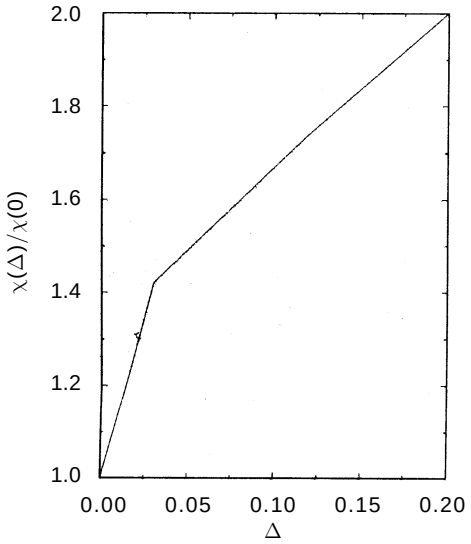

Figure 1. Plot of diamagnetic enhancement with Δ.

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